

NISTIR 6242

ANNUAL CONFERENCE ON FIRE RESEARCH
Book of Abstracts
November 2-5, 1998

Kellie Ann Beall, Editor

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U.S. Department of Commerce
William M. Daley, *Secretary*
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Gary Bachula, *Acting Under Secretary for Technology*
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The Molecular Level Design of Flame Retardants and Fire Resistant Materials

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Recent work conducted in this laboratory has demonstrated the application of molecular modeling techniques to the design of flame retardants and fire resistant materials [1-5]. This effort has culminated in the development of a novel computer program, hereafter called MD_REACT, that simulates the thermal degradation of polymers (see Figure 1). The basis of this model is molecular dynamics (MD), which consists of solving Newton's equations of motion for each of the $3N$ degrees of freedom associated with the model polymer. The feature that distinguishes MD_REACT from other MD codes is that it allows for the formation of new bonds from free radical fragments that are generated when bonds in the polymer break and, thereby, accounts for the chemical reactions that play a major role in the thermal degradation process [6].

Bond dissociation and formation are simulated in MD_REACT by the following algorithm. A list of the free radical sites, that are generated when bonds in the polymer break, is updated at every time step. These free radicals are eligible to react with each other to form new bonds. The specific criterion used in MD_REACT is that covalently bonded atoms become free radicals when their potential energy comes within a few $k_B T$ of the bond dissociation energy. The program generates a new set of bonds, consisting of all possible covalent interactions between the available free radicals and retains those corresponding to the lowest energy subject to the constraints imposed by the rules of atomic valence.

The motivation behind the development of MD_REACT was to create a versatile model that could be used to study thermal degradation at a molecular level in a wide range of polymers. The strategy employed to accomplish this objective was to interface our program for performing reactive dynamics on simple vinyl polymers [2] with Discover 95 [7], a commercially available molecular dynamics code offered by Molecular Simulations (MSI). The interface between the programs is established using an inter-process communication protocol (IPC) to pass coordinates, forces and connectivity information between MD_REACT, which computes the reactive forcefield, and Discover 95, which updates the molecular structure on the basis of the solution to the equations of motion.

In order to extract meaningful information, the disparity between the time scales associated with laboratory measurements, such as the cone calorimeter (seconds) and those accessible to atomistic simulations (picoseconds) must be overcome. Our solution is to substitute the rate constants for random scission initiation (k_i), propagation (k_p), and termination (k_t) obtained from our computer simulations into a simple kinetic model [8]. The first step in this process is to generate a population of free radical polymer fragments. This is accomplished by performing simulations at very high temperatures (usually in excess of 2000 K). The resulting structures are then used to initiate the second stage of the computer experiment, the purpose of which is to simulate the propagation and termination reactions. These simulations can actually be performed at realistic thermal degradation temperatures (typically, 873 K) because the

activation energies for the β -scission reactions, corresponding to propagation (C-C scissions) and first order termination (C-H scissions), are comparatively low. The global rate of mass-loss is computed using the values of k_p and k_t , obtained directly from the results of the second stage simulations, and a value of k_i , which is extrapolated to thermal degradation temperatures using the kinetic parameters obtained by fitting the temperature dependence of the rates of random scission observed in a series of high temperature simulations. The global rates of mass-loss obtained in this way will be compared to the results of TGA and radiative gasification experiments performed on polypropylene and related polymers.

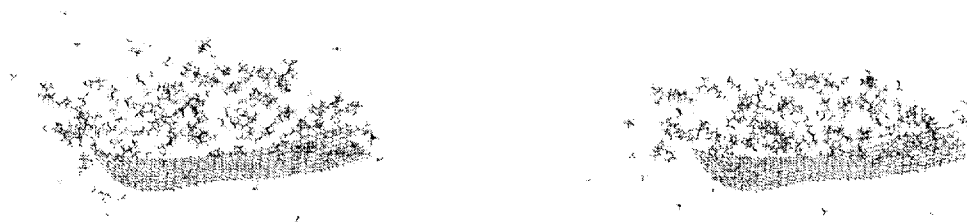


Figure 1. Frames from the simulated thermal degradations of polypropylene (left) and a polypropylene/graphite(right) nanocomposite.

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7. Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by NIST.
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